Effect of an Ionomer on the Mechanical Performance of Flame Retardant ABS Formulations

Zeynep Yurdakul[1], Vera Realinho[2], M. Antunes[2], Süheyla Aydın[3], Jose Ignacio Velasco[2]

[1]*Sabancı University, Materials Science and Nanoengineering, Istanbul, 34956, TURKEY*

[2]*Centre Català del Plàstic. Universitat Politècnica de Catalunya, BarcelonaTech (UPC), Departament de Ciència dels Materials i Enginyeria Metal.lúrgica C/Colom 114, E-08222, Terrassa, SPAIN*

[3]*Istanbul Technical University, Department of Metallurgical and Materials Engineering, Istanbul, 34469, TURKEY*

Abstract

Acrylonitrile butadiene styrene (ABS) is a widely used thermoplastic copolymer due to its desirable properties such as good mechanical performance (toughness, impact resistance, among others), ease of processability, chemical resistance, and low cost. Nevertheless, the major drawback of ABS is its inherent flammable characteristic which could restrict its use in a wide variety of applications where fire retardancy is required. Phosphorus flame retardants (PFRs) have been utilized in the last decade in ABS as a more environmentally friendly option compared with its halogenated counterparts. Nevertheless, one of the main drawbacks of incorporating PFRs into ABS is normally the deterioration of its mechanical performance. The use of an ionomer, as a compatibilizer, is the strategy proposed in the present work to reduce the negative effect of PFRs on ABS mechanical performance. In this study, two different PFR additives, selected regarding to high efficiency of flame retardant effect on ABS, and a commercial ionomer were incorporated into ABS by means of a melt blending process. Hence, the effect of adding a commercial ionomer on the ABS and ABS phosphorus flame retardant (PFR) formulations (ABS-PFR) was analyzed by means of different characterization techniques.

1. Introduction

Acrylonitrile butadiene styrene (ABS) copolymer is a thermoplastic produced by combining three monomers: acrylonitrile, butadiene, and styrene. The ratio between these monomers and the molecular structure of the ABS can be manipulated to produce goods with useful characteristics. ABS consists of two phases: a continuous phase of styrene-acrylonitrile (SAN) copolymer, and a dispersed phase of polybutadiene particles. Both phases promote the specific characteristics of the ABS polymer. SAN phase combines the easy processing of polystyrene with the stability and chemical durability of acrylonitrile. On the other hand, the incorporation of butadiene rubber into ABS copolymer promotes high impact strength characteristics. Beside these properties, the most important drawback of ABS is its inherent flammability behavior, like most of the styrene-based polymers [1, 2].

Many strategies are provided to improve the fire resistance of ABS, but due to environmental protections, halogen free PFRs are a preferable solution. However, the high content (20-30 wt.%) of PFR required to achieve flame retardancy leads to a deterioration of styrenics copolymers mechanical performance [3, 4, 5].

Compatibilizers are suitable candidates to improve blends miscibility and mechanical properties of flame retardant polymer formulations. Ionomers are a unique type of compatibilizers that have a small molar fraction (typically less than 10 mol %) of ionic groups covalently bonded to the polymer structure [6, 7]. The ionic cluster region of ionomers behaves as thermoreversible crosslinks and improves the toughness, melt viscosity, and adhesion properties of the copolymers [8-12].

In the present work, ABS and flame retardant ABS formulations were prepared and the effect of adding a commercial ionomer on the ABS and ABS phosphorus flame retardant (PFR) formulations (ABS-PFR) was analyzed. The main objective of this study was to analyze to effect of a commercial ionomer on the thermal stability and mechanical behaviour of ABS-PFR formulations.

2.Experimental Procedure

2.1. Materials

ABS pellets (ELIXTM 128 IG) was acquired from ELIX Polymers which have white to slightly yellowish color and the butadiene content of ABS is 26-28 %. PB with the commercial name BUNA CB 565 T, manufactured by LANXESS, was used.

BUNA CB 565 T is solid transparent rubber with a density of 0.91 g/cm^3. Ethylene methacrylic acid (EMAA) copolymer (commercial name Surlyn® 8140 and density of 0.96 g/cm^3), were supplied by Dupont™, was used as a commercial ionomer. Phosphorus flame retardants were APP (Clariant, Exolit® AP 422 and density of 1.9 g/cm^3) and AlPi (Clariant, Exolit® OP 1230 and density of 1.35 g/cm^3) which were used to obtain flame retardant characteristic in polymer formulations.

2.2. Preparation of Formulations and Specimens

In this study, all formulations were prepared by melt compounding in accordance with the different components using a Brabender PlastiCorder static mixer, at a temperature and screw speed of 165 ºC and 30 rpm respectively, with a mixing time of 15 minutes. A 10 and 20 wt.% of an ammonium polyphosphate (APP) and an aluminium diethylphosphinate (AlPi) were added, in a 1:1 proportion, into ABS. Also, a 5 per hundred of resin (PHR) of an ionomer of ethylene methacrylic acid copolymer (EMAA) was incorporated into the ABS and ABS phosphorus flame retardant (PFR) formulations.

In order to prepare the specimens, a hot-plate press (IQAP-LAP PL15) was used with 4 mm thick square mold, by heating at 165 ºC applying a pressure of 10-100 bar.

2.3. Testing Procedure

The morphology of the formulations was analyzed to use JEOL JSM-5610 by applying a voltage of 15 kV. Samples were previously prepared by machining and brittle fracturing with final sputtering of a thin layer of gold onto the fractured surface in argon atmosphere using a BAL-TEC SCD005 Sputter Coater.

The thermal analysis of ABS PFR formulations were done by means of a thermogravimetric analysis (TGA). A Mettler Toledo TGA/DSC 1 STAR System was utilized in this study in order to evaluate the thermal decomposition of polymeric materials. During this process, a nitrogen atmosphere was used and a heating rate of 10 °C minute from 30 °C to 1000 °C was applied. The weight of all samples was between 12 to 14 mg.

Flexural tests were done by a using three-point bending test (Galdabini Sun 2500) according to ISO 178 standards to measure flexural modulus in order to analyze the effects of the ionomer on the mechanical properties.

The Ceast® Resil Impactor Junior impact test machine was used to determine the impact strength of samples. The samples were prepared according to ISO 179-1:2000 normative.

3. Results and Discussion

3.1. Morphological Analysis

The samples were analyzed by SEM to investigate ionomer effects on the fracture surface of ABS flame retardant formulations.

In Figure 1., the smooth APP parts and rough phosphinate salt particles are seen in the micrographs. The APP particles were covered with ionomer instead of phosphinate salt particles. Ionomer seems to behave as a linking agent and improve the compatibility between matrix and APP.

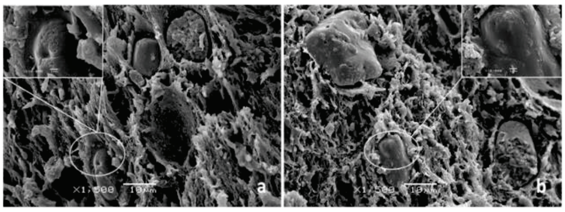

Figure 1. SEM micrographs of a) ABS-I-PFR 10, b) ABS-I-PFR 20 samples.

3.2. Thermal Analysis

The starting temperature of decomposition decreased with the presence of the PFR additives are presented in Table 1. An increase of residue was also observed according to an increase of wt.% PFR at 900 °C.

Table 1. Flexural test results of ABS PFR samples.

Sample	**$T_{5\ wt.\%}$ (°C)**	**Residue (wt.%)**
ABS-PFR 10	359	4.74
ABS-PFR 20	344	8.02
ABS-I-PFR 10	324	5.26
ABS-I-PFR 20	310	8.76

The inclusion of ionomer in PFR formulations increased the amount of residue and decreased the degradation starting temperature as can be seen in Figure 2. The decrease of the onset temperature could indicate a catalyzer effect of the ionomer on the decomposition of the PFR additives.

3.3. Mechanical Analysis

3.3.1 Flexural Test

The flexural test results of samples are seen in Table 2. It is seen that the maximum flexural strength decreased with the increase of PFR content. The reason of the decrease of the maximum flexural strength could be due to the increase of poor interface between PFRs and polymer matrix. Additionally, the increase of flexural modulus is related to the increase of PFR loading. Despite the negative effect of the PFR addition, ionomer added samples have higher modulus and strength than the samples without ionomer. The inclusion of ionomer enhances the maximum flexural strength of flame retardant samples; this could be related with the high compatibility between APP and polymer matrix.

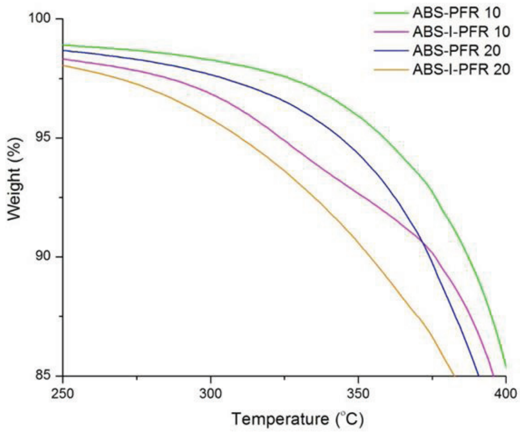

Figure 2. Amplification of starting of degradation step for ABS-PFR 10, ABS-I-PFR 10, ABS-PFR 20 and ABS-I-PFR 20 formulations.

Table 2. Flexural test results of ABS PFR samples.

Sample	Max. Flexural Strength (MPa)	Flexural Modulus (GPa)
ABS	27.08 ± 0.27	0.773 ± 0.001
ABS-PFR 10	24.45 ± 1.77	0.820 ± 0.015
ABS-PFR 20	21.61 ± 1.28	0.857 ± 0.010
ABS-I-PFR 10	26.99 ± 0.25	0.856 ± 0.007
ABS-I-PFR 20	24.28 ± 1.51	1.003 ± 0.004

3.3.2 Charpy Impact Test

The charpy impact strength of the flame retardant ABS formulations is shown in Table 3. The impact strength of neat ABS is 25.7 kJ/m^2. It can be proved that the charpy impact strength is significantly lowered with the addition of the different flame retardant additives.

Table 3. Impact test results of ABS PFR samples.

Sample	Impact Strength (kJ/m^2)
ABS-PFR 10	18.7 ± 2.4
ABS-PFR 20	12.2 ± 2.7
ABS-I-PFR 10	6.4 ± 0.8
ABS-I-PFR 20	4.0 ± 0.9

The high value of ABS is due to the fact that it is a hard and tough thermoplastic terpolymer with good impact strength; but impact strength is very sensitive to fillers or additives.

4. Conclusion

The results of this study provided a clearer understanding of the ionomer effect on mechanical properties of ABS PFR formulations. The morphology of the fracture surface of the samples was analyzed by means of scanning electron microscopy (SEM). Poor interaction between PFR additives and matrix was reported for samples without ionomer. On the other hand, the ionomer addition enhanced the interaction between APP and polymer matrix. This indicated that ionomer addition could partially compatibilize PFR additives and ABS matrix. The thermogravimetric analysis of ABS formulations showed that the starting temperature of decomposition of ABS decreased with the presence of the PFR additives. An increase of residue was also observed in accordance with an increase of wt.% PFR. This observation could be attributed to synergistic interactions between the polymer matrix and the PFR additives during the thermal decomposition process. In addition, according to TGA results, inclusion of ionomer in PFR formulations increased the amount of residue and degradation starting temperature. The mechanical properties of flame retardant polymers were investigated by using three-point bending flexural test and charpy impact test in accordance with inclusion of ionomer. Analysis showed that the formulations with ionomer presented higher flexural modulus. Impact strength of ABS flame retardant formulations decreased with increasing wt.% PFR. Analysis also showed that ionomer addition decreased the impact strength of the samples.

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